

## Heavy Vehicle Propulsion Materials

# Catalysts by First Principles

### Background

The high loading of precious metals to overcome gradual and persistent deterioration of the performance of three-way catalysts for after-treatment of engine out emissions is rather well-known. This deterioration has been found to be rapid in supported catalyst systems that operate under oxidizing environment (e.g., lean  $\text{NO}_x$  traps, oxidation catalysts, HC-SCR, etc.). However, alleviating performance deterioration through the traditional catalyst development approach has not been successful in this instance.

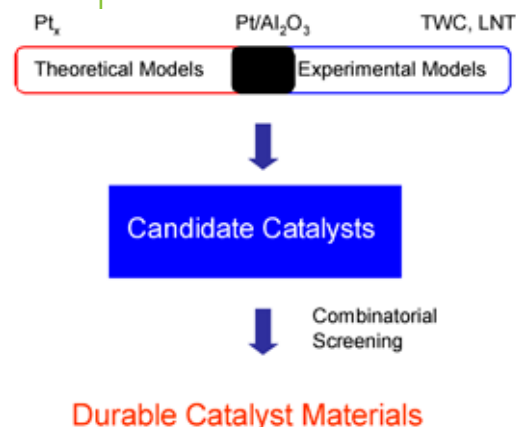
Despite dramatic improvements in experimental and theoretical bases for their characterization, the traditional approach to catalyst development is still dominated by trial and error methods. Although it has been successful, the empirical development of catalytic materials is time consuming and expensive and brings no guarantees of success. In addition, experimental catalysis has not benefited from the advances in high performance computing that enables more realistic simulations (empirical

and first-principles) of large ensemble atoms including the local environment of a catalyst site in heterogeneous catalysis.

Thus, a protocol to systematically find the optimum catalyst can be developed that combines the power of theory and experiment in an iterative process for atomistic design of catalytically active sites and can directly translate the fundamental insights gained to a complete catalyst system that can be technically deployed (shown in Figure 1).

### Technology

The theoretical modeling is based on DFT studies of Pt clusters to understand the relationship between cluster size, structure, composition, and reactivity. This, coupled with first-principles thermodynamics, provides insights into the effects of oxidizing atmosphere ( $\text{O}_2$ ) – finite ( $T$ ,  $p\text{O}_2$ ), structure, composition, redox potential on



**Figure 1.** A protocol that combines the power of theory and experiment in an iterative process to systematically find optimum catalysts.

### Benefits

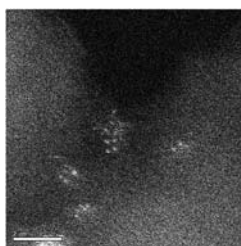
- Enables faster, less expensive catalyst development.
- Determination of reactive catalyst site structure enables design of durable catalysts with optimal operation.



particle size. The results provide guidance for investigations of larger/supported clusters. Experimentally, researchers have synthesized a series of Pt and Re clusters and particles supported on morphologically different  $\gamma$ -aluminas. The microstructural characterization reveals structural differences in 1-3 atom and 10-20 atom clusters.

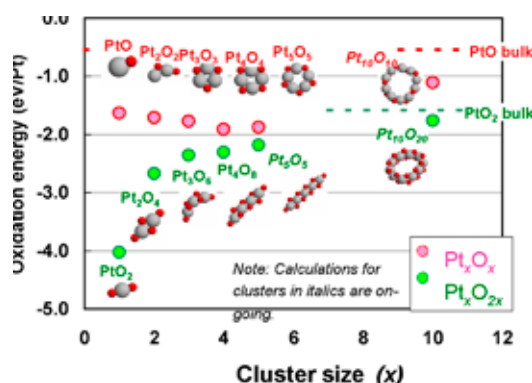
Theoretical models reveal that Pt nanocluster reactivity shows strong size dependence. Small clusters are much more prone to oxidation and oxidized clusters adopt 1-D or 2-D structures. Higher temperature or lower  $pO_2$  leads to less oxidation and lower oxide phases are more prevalent for larger clusters. Increasing temperature leads to increased oxidation of Pt oxide clusters but reduction of clusters becomes more facile.

Experimentally, researchers have synthesized a variety of stabilizer incorporated aluminas with controlled surface properties (e.g., sol-gel, mesoporous molecular sieves etc.) that are stable to thermal treatment ( $\sim 900^\circ\text{C}$ ). The synthesis and characterization of carbonylated, decarbonylated, and nanoclusters of precious metals (Pt, Re) on these aluminas have also been completed. Figure 2 shows 10-20 atom Pt nanoclusters on  $\gamma$ -alumina. This structure is an input for theoretical modeling of Pt/ $\gamma$ -alumina materials.



**Figure 2.** HA-ADF image from the STEM showing Pt particles.

(carbonylated, decarbonylated, and nanoclusters) on  $\gamma$ -alumina (commercial, sol-gel, and mesoporous molecular sieve) are currently being examined for the oxidation of CO, HC, and  $\text{NO}_x$  to determine the structure of reactive catalyst sites. This iterative process will lead to the identification of optimal catalyst sites for CO, HC, and  $\text{NO}_x$  oxidation. These results will enable the design of durable catalysts containing such sites for optimal operation.



**Figure 3.** Oxidation energies of the  $\text{Pt}_x\text{O}_x$  and  $\text{Pt}_x\text{O}_{2x}$  clusters.

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## A Strong Energy Portfolio for a Strong America

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## Status

The reactivity of precious metals